



# Controlled modification of Pt/Al<sub>2</sub>O<sub>3</sub> for the preferential oxidation of CO in hydrogen: A comparative study of modifying element

Shailesh K. Jain<sup>a</sup>, Eleanor M. Crabb<sup>a,\*</sup>, Lesley E. Smart<sup>a</sup>, David Thompsett<sup>b</sup>, Andrew M. Steele<sup>b</sup>

<sup>a</sup> Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

<sup>b</sup> Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH UK

## ARTICLE INFO

### Article history:

Received 16 September 2008

Received in revised form 11 December 2008

Accepted 14 December 2008

Available online 25 December 2008

### Keywords:

PROX

Platinum

Promoted catalysts

## ABSTRACT

The catalytic performance of a series of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, modified with Cr, Mn, Fe, Co, Ni, Cu and Sn, has been tested for the preferential oxidation of CO in hydrogen. The promoters were deposited onto the surface of a 5 wt.% monometallic Pt/Al<sub>2</sub>O<sub>3</sub> catalyst using a controlled surface approach, to give a nominal promoter:Pt surface atomic ratio of 1:2 (corresponding to typically 0.15–0.25 wt.% of the promoting metal). The aim of this approach was to selectively create the Pt-promoter oxide interfacial sites considered to be important for the non-competitive dual-site mechanism proposed for such promoted catalysts. In this mechanism the promoting oxide is believed to act as an active oxygen provider, providing oxygen for the oxidation of the CO on the Pt. The catalysts were characterised using TEM, EDX, ICP-AES and CO chemisorption and results suggest that the promoter was successfully deposited on to the Pt surface. Even at the low loadings of promoter used, significant enhancement was observed in the catalytic performance of the PROX reaction in a simulated reformat mixture, for the Fe- and Co-promoted catalysts in particular (and to a lesser extent the Mn, Sn, Cu- and Ni-promoted catalysts), highlighting the successful preparation of the Pt-promoting metal oxide interfacial sites. The Mn-promoted catalyst, however showed no enhancement in the absence of water suggesting that the form of the promoting metal oxide may be particularly important for promotion of Pt for the PROX reaction.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Proton exchange membrane fuel cells (PEMFC) and Phosphoric acid fuel cells (PAFC) have been studied extensively in recent years, showing considerable promise for both stationary and automotive power supply. These fuel cells typically use the electrochemical reaction between hydrogen, as the fuel, and air or oxygen, as the oxidant. The hydrogen fuel can be supplied by reforming of hydrocarbon fuels such as methanol, natural gas and gasoline, however the hydrogen obtained contains low levels of CO as an impurity. CO is a poison for the Pt electrocatalyst in the fuel cell and so, for efficient working of the fuel cell, the hydrogen feed needs to contain less than 10 ppm CO.

The majority of the CO in the reformat can be removed using the water gas shift reaction (reaction (1)):



followed by the selective or preferential oxidation (PROX) of CO (reaction (2)) (avoiding oxidation of the hydrogen (reaction (3)))

to give levels suitable for the fuel cell.



A large number of catalysts have been studied for the PROX reaction and some of the most interesting systems combine both a noble metal and a reducible oxide, such as CoO<sub>x</sub>, FeO<sub>x</sub>, MnO<sub>x</sub> or CeO<sub>x</sub> [1–12]. Examples include Pt supported on the reducible oxide itself or alumina or silica supported Pt promoted by the oxide. A dual-site mechanism is believed to be important for these catalysts, with CO adsorption on the Pt and the oxide providing sites for the adsorption/dissociation of oxygen [2,3]. The presence of adsorbed H<sub>2</sub>O/OH species may also be important [8–10]. Interaction between the adsorbed CO and ‘active’ oxygen is believed to occur at the interface of the Pt and oxide, or by oxygen spillover onto the Pt sites [2], with the ‘active’ oxygen being replenished by reoxidation by oxygen from the gas phase [3].

In these oxide promoted catalysts, the activity is likely to be controlled via the Pt-oxide interface and so it is imperative that the oxide and Pt should be associated together to maximize the CO conversion [3,4]. This can be difficult to ensure using conventional

\* Corresponding author. Tel.: +44 1908 659894.

E-mail address: [e.m.crabb@open.ac.uk](mailto:e.m.crabb@open.ac.uk) (E.M. Crabb).

preparation methods such as impregnation or co-precipitation, where the different components may be deposited at separate sites on the support. Even if some of the components are deposited together, it can be difficult to determine the optimum ratio and differentiate between surface effects and bulk effects of the different components. One way to avoid this is to use a controlled surface modification technique to selectively deposit the promoter where it is required, in close association with the noble metal. This has been achieved using selective vapour deposition, for example using vaporisation of alloy rods of the noble metal and promoting metal [13]. An alternative is to use a selective reaction between a precursor of the promoter (in solution) and hydrogen adsorbed on the surface of the platinum monometallic catalyst. Such a method should facilitate creation of the “ideal” interfacial sites between the promoter and the metal surface. We have successfully prepared a range of promoted carbon and alumina supported Pt catalysts using such a method [14–18].

The work reported in this paper forms a part of a study modifying alumina supported Pt catalysts with a number of different metal oxides. Previous studies for promoted catalysts prepared using this surface modification technique have suggested that the promoter exists as a dispersed oxide after the final preparation step upon exposure to air [14–18]. Thus this work should enable a study of the Pt/metal oxide interface without significant effects from the bulk oxide. The modified catalysts were examined for their performance towards the selective oxidation of CO in the presence of excess hydrogen and compared to that of the corresponding parent monometallic catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

A proprietary 5 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with a Pt dispersion of 29% was provided by Johnson Matthey (UK). The syntheses of bimetallic catalysts were carried out in a specially designed reactor and saturator. The monometallic Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was loaded into a glass reactor and purged with nitrogen for half an hour to remove any air from the system. It was then reduced under flowing hydrogen (flow rate: ~100 cm<sup>3</sup> min<sup>-1</sup>) at 200 °C for 3 h before cooling down to room temperature under an atmosphere of hydrogen. The required amount of the organometallic precursor was dissolved in heptane or toluene (see Table 1) then added to the saturator and purged with nitrogen for 20 min. The contents of the saturator were then transferred under nitrogen into the reactor containing the reduced Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Hydrogen gas was passed through the reactor and the reaction carried out at room temperature for about 12 h and then at approximately 95 °C for a further 8–12 h. The reaction was monitored by analyzing the exit gas using a gas chromatograph. After the reaction, the contents of the reactor were discharged, filtered, and washed repeatedly with heptane to remove any unreacted precursor. The dried catalyst was transferred into the reactor and purged with nitrogen gas for 30 min to remove air from the system. The contents of the reactor

were then reduced under flowing hydrogen at 200 °C for 3 h, and finally flushed with nitrogen for at least 20 min, before exposing to air, to prevent combustion. The loading of the promoting species was chosen to represent a theoretical surface coverage of the monometallic noble metal surface sites (based on the number of accessible surface sites determined by chemisorption (29%)) equivalent to half a monolayer (M:Pt surface atomic ratio 1:2) for the series of catalysts tested, and a full monolayer for selected samples (M:Pt surface atomic ratio 1:1).

### 2.2. Characterisation

The assays of the promoted Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The accessible fraction of the metal surface available for the reaction was determined using volumetric chemisorption of carbon monoxide in a conventional pyrex vacuum system with a vacuum pressure of 10<sup>-5</sup>/10<sup>-6</sup> mbar. In a typical experiment, approximately 0.1 g of the catalyst was outgassed at 250 °C for 30 min and then allowed to cool to room temperature. The sample was reduced under 750 mbar pressure of hydrogen at 350 °C for 30 min and then outgassed at the same temperature for a further 30 min. The furnace was removed and outgassing was continued until the sample cooled down to room temperature at which point the chemisorption experiments were performed. A pressure range of 0–50 mbar was used for all the catalysts. The dispersion of the catalysts was calculated from the amount of adsorbed gas (*Q*<sub>0</sub>) which was calculated from the adsorption isotherm by extrapolating the linear region of isotherm back to zero pressure.

The transmission electron micrographs were obtained on model FEI Tecani F20 (S-Twin), operating at an accelerating voltage of 200 kV. EDX analysis was carried out using an EDAX Si(Li) detector. The instrument was also fitted with an ultra-high resolution STEM high angle annular (HAADF) detector with magnification range up to 10,000 kx and the point resolution of 0.24 nm. The Fe- and Sn-modified catalyst samples were prepared by dipping a Cu-grid (Holey carbon film on 300 mesh) into a sonicated dispersion of the sample in deionised water. The Co-modified catalyst samples were prepared as a very fine powdered layer of the catalyst on a Cu-grid.

### 2.3. Catalyst testing

#### 2.3.1. Dry tests

The catalysts were tested for the oxidation of carbon monoxide in the presence of excess hydrogen in a fixed-bed laboratory reactor under a gas mixture containing 1.25% O<sub>2</sub>, 0.5% CO, ~25% H<sub>2</sub> and the balance N<sub>2</sub>. The total flow rate of the reaction gas was maintained at 100 cm<sup>3</sup> min<sup>-1</sup>. All the catalysts were diluted to one-fifth with the alumina support material. Approximately 70 mg of the diluted catalyst under examination was pretreated under the 2% CO/H<sub>2</sub> mixture at 40 °C for 40 min, prior to each test. The reaction products were analyzed using a gas chromatograph (Ai Cambridge GC 94) fitted with a TCD with Molecular Sieve 5A 100–120 mesh. A CO<sub>2</sub> sensor (Servomex Analyzer Series 1400) was also used to analyze the amount of CO<sub>2</sub> in the output. Results were found to be consistent until at least 350 °C.

The term, ‘CO, O<sub>2</sub> consumption (vol %)’ is defined as the amount of CO and O<sub>2</sub> (in vol %) initially present in the gas mixture consumed during the reaction (by analysis).

The selectivity towards CO<sub>2</sub> was calculated as the ratio of the desired reaction (CO oxidation) to the overall O<sub>2</sub> consumption:

$$\text{Selectivity} = \frac{\text{Amount of oxygen used in CO oxidation}}{\text{Total amount of oxygen consumed in the reaction}} \times 100$$

**Table 1**  
The precursors used in this study.

System	Precursor used
(1:2)CrPt	Cr(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>
(1:2)MnPt <sup>a</sup>	Mn(II)-acetylacetonate
(1:2)FePt	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>
(1:2)CoPt	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>
(1:2)CuPt <sup>a</sup>	Cu(II)-acetylacetonate
(1:2)SnPt	Sn(n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub>
(1:2)NiPt	Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>

<sup>a</sup> Catalyst preparation carried out in toluene.

**Table 2**

Elemental analysis of the catalysts prepared.

Catalyst	Pt assay (Mass%)	Experimental %M (Mass%)	Theoretical %M <sup>a</sup> (Mass%)	CO/Pt <sup>b</sup>
5%Pt/Al <sub>2</sub> O <sub>3</sub>	5.18	–	–	0.29
(1:2)CrPt	4.79	0.17	0.25	0.13
(1:2)MnPt	4.84	0.19	0.22	0.11
(1:2)FePt	4.62	0.20	0.22	0.16
(1:1)FePt	4.73	0.38	0.40	0.17
(1:2)CoPt	4.89	0.16	0.20	0.19
(1:1)CoPt	4.99	0.34	0.46	0.20
(1:2)CuPt	4.91	0.23	0.22	0.20
(1:2)SnPt	4.49	0.44	0.40	0.13
(1:1)SnPt	4.65	0.88	0.91	0.08
(1:2)NiPt	4.93	0.23	0.22	0.20

<sup>a</sup> Estimated according to the mass of precursor and 5%Pt/Al<sub>2</sub>O<sub>3</sub> used and the Pt dispersion (29%).<sup>b</sup> CO/Pt refers to the fraction of Pt sites accessible to CO on the surface of the catalyst calculated from CO chemisorption studies.

### 2.3.2. Wet tests

The catalysts were also screened under a simulated reformat gas mixture at the Johnson Matthey Technology Centre, Sonning Common, UK. Prior to the tests, the catalyst was pelletized, crushed and sieved to obtain particles in the 250–355  $\mu\text{m}$  size range. Approximately 50 mg of the catalyst was mixed with approximately 150 mg of cordierite and loaded into the reactor. For these studies, the gas composition was set to 60% H<sub>2</sub>, 0.1% CO, 20% CO<sub>2</sub>, 0.15% O<sub>2</sub> and balance nitrogen. The temperature of the reactor was maintained at 150 °C throughout the experiment. Once the temperature of the reactor reached 150 °C, 10% H<sub>2</sub>O was added to the feed and the catalyst was left for 60 min to stabilise. The total flow rate during this stabilisation period was maintained at  $3 \times 10^4 \text{ cm}^3 \text{ min}^{-1}$ . During this period, both CO and O<sub>2</sub> were monitored in order to note any deactivation of the catalyst. After about 60 min, the amounts of CO and O<sub>2</sub> consumed were followed as a function of space velocity. Space velocity is defined as the amount of gas flowing (in  $\text{cm}^3$ ) per unit time (in h) per unit mass (in g) of the catalyst loaded into the reactor. The space velocity was varied by changing the flow rate of the gas mixture. The tests were started at a space velocity of  $2 \times 10^6 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$  over the catalyst, gradually increasing stepwise up to about  $3 \times 10^7 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ .

## 3. Results and discussion

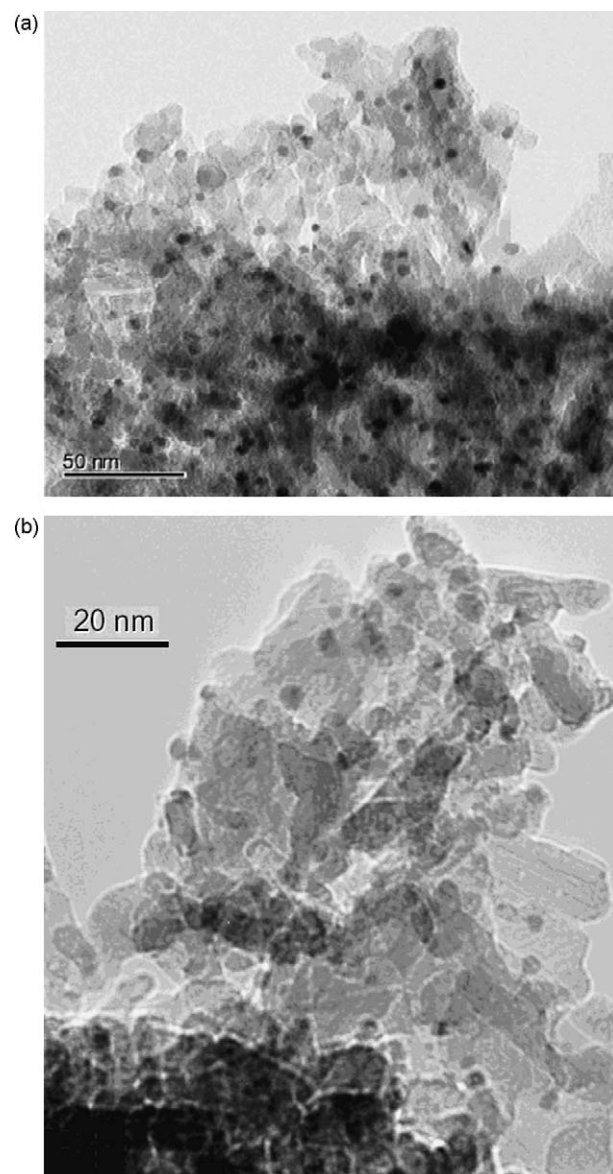
### 3.1. Catalyst characterisation

A list of the modified catalysts examined in these studies is given in Table 2. The metal loadings determined from ICP-AES analysis and the dispersion values obtained from the CO chemisorption experiments for these catalysts are also included.

A comparison of the theoretical and experimental assays of second metal indicates, considering experimental error, that almost all of the second metal was deposited on to the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, for all the promoters with the exception of chromium. Incomplete reaction in this case was likely to be due to the decomposition of the chromocene precursor during the course of the reaction, which was subsequently washed away during the filtering process.

Inspection of the CO chemisorption results (Table 2) indicates a decrease in the volume of CO adsorbed by the promoted catalysts compared to the parent monometallic catalyst. Assuming that each component retains its bulk properties, the CO uptake by the promoted catalysts can be attributed solely to the noble metal. An identical preparative procedure, but without a second metal precursor, resulted in no significant difference in the dispersion value of the monometallic platinum, indicating that no significant sintering has occurred during the preparation procedure itself [14]. Assuming that the stoichiometry of adsorption of CO is not significantly influenced by the addition of the second metal, the

results suggest that the number of surface sites available for CO chemisorption has decreased upon addition of the promoter. This is similar to the results generally obtained for catalysts prepared using this type of technique [14–16,19–21]. The decline in the



**Fig. 1.** Typical transmission electron micrographs of (a) 5%Pt/Al<sub>2</sub>O<sub>3</sub> and (b) (1:2)CoPt/Al<sub>2</sub>O<sub>3</sub>.

amount of CO chemisorbed can be attributed to a geometric effect resulting from physical blockage of the platinum group metal atoms by the second metal and can be interpreted as evidence for the deposition of the promoter on to the surface of the platinum. For the catalysts prepared with a nominal surface coverage of the Pt by the promoter of half a monolayer, we would expect the CO uptake of the promoted catalysts to be approximately half that of the unpromoted catalyst, as indeed was the case for the majority of the catalysts prepared. However, for the Fe- and Co-modified catalysts (but not the Sn), there was little difference between the results for the (1:2) and (1:1) catalysts. These results suggest that as an increasing amount of the second metal is deposited, the metal may interact with the deposited metal sites themselves rather than the Pt leaving some free Pt sites accessible, that the second metal may migrate onto the support or that the  $\text{MO}_x$  sites (possibly in association with the Pt) may adsorb CO themselves. The promoter may also influence the CO adsorption properties of the Pt [3,22,23].

Typical transmission micrographs for selected catalysts are shown in Fig. 1. The 5%Pt/ $\text{Al}_2\text{O}_3$  catalyst sample was well dispersed with no indication of agglomeration of the Pt particles (Fig. 1a). The particle size was found to be in the range 2–7 nm with the majority of diameter 4–5 nm. Micrographs of the  $\text{FeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{CoO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalysts, (illustrated in Fig. 1b for (1:2)  $\text{CoO}_x/\text{Pt}/\text{Al}_2\text{O}_3$ ) indicated that the particle size of the catalysts did not increase significantly on addition of the second metal. No evidence of sintering was found for any of the catalysts.

In order to confirm the location of the two metals relative to each other, the HAADF imaging technique was used for  $\text{CoO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalysts prepared. A line scan (20–50 nm) was selected and EDX analysis performed along the selected line. The analysis confirmed that the position of the two metals coincides, with Co found only at the positions where Pt was also present. No cobalt particles were found on the support. The results are illustrated in Fig. 2 for the (1:2) $\text{CoO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalyst. Similar results were found for the  $\text{FeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{SnO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalysts using EDX analysis, with evidence that the Fe or Sn and the Pt were in close proximity and again no evidence for the presence of isolated particles of the second metal.

We have shown previously from EPR studies of Fe modified Pt/ $\text{Al}_2\text{O}_3$  catalysts prepared using this technique, that upon exposure to air after the final reduction step in the preparation, the particles contain platinum in association with oxidized iron, suggesting partial coverage of the platinum particles with dispersed  $\text{FeO}_x$  [14]. The amount of Fe(III) and/or Fe(II) present depended critically on whether the catalyst was under reducing or oxidizing conditions. XANES analysis of a range of ceria promoted catalysts prepared using the same technique has also shown the presence of Ce(IV) and Ce(III), the exact ratio again depending on the oxidizing/reducing gas mixtures used, as well as the presence of the Pt surface [18]. XPS studies of Sn and Ge modified Pt/C catalysts prepared using the same technique showed the presence of Sn(II) and/or Sn(IV) (it is not possible to distinguish between these tin species using XPS), with no evidence of any Sn(0) present, and Ge(IV) respectively [15,16]. A similar conclusion was drawn by Sánchez Sierra et al. [24] for  $\text{GeO}_x/\text{Ru}/\text{Al}_2\text{O}_3$  prepared using a similar technique who concluded that their ruthenium particles were partially covered by a layer of  $\text{GeO}_x$ . It is unlikely that there is alloy formation between the promoting metal and Pt at the reduction temperature used in this study (200 °C). Although the EPR study above showed evidence of  $\text{Fe}^0$  in close association with Pt under hydrogen, on exposure to air the Fe was found to be readily oxidized [14]. Similarly EXAFS studies at the Fe or Co K edge of a range of Fe and Co modified Pt/C catalysts prepared using the same technique showed evidence of Pt neighbours in the first coordination shell after treatment at 200 °C under hydrogen, which were not evident after treatment at 200 °C in air [18].

Thus, we predict from our characterisation studies that the promoted catalysts prepared exist as platinum with a partial overlayer of the promoting metal oxide, the exact oxidation state of which depends on the promoting metal itself and the environment to which it is exposed. Due to the low loadings of the promoter and the nature of the preparation technique, the promoting oxides are likely to be present as a dispersed oxide in contact with the Pt and not as the bulk oxide. The underlying Pt in turn is likely to influence the extent of oxidation of the dispersed oxide compared to its bulk oxide [11,18].

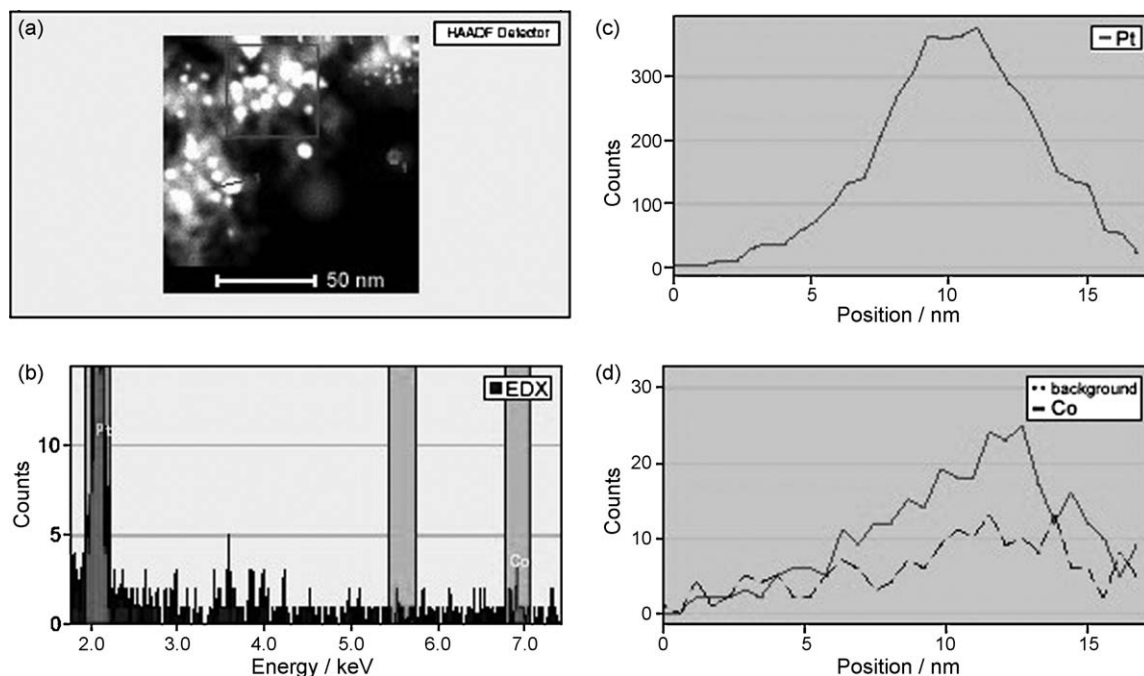


Fig. 2. A typical (a) HAADF image and (b) EDX analysis of (1:2)  $\text{CoPt}/\text{Al}_2\text{O}_3$  catalyst (with element specific line profiles for (c) Pt and (d) Co).



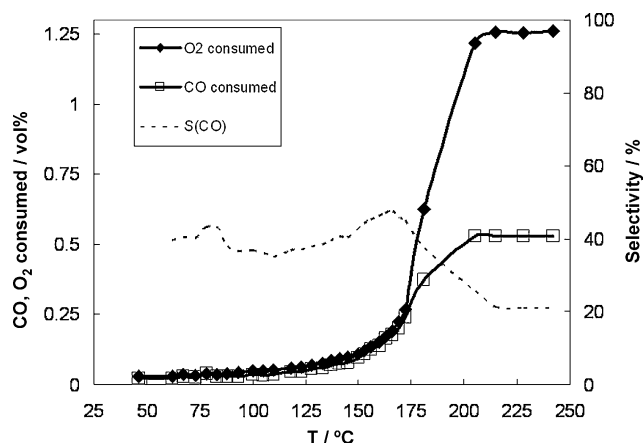


Fig. 3. The consumption of CO and O<sub>2</sub> on 5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in  $\lambda_5$  gas mixture.

### 3.2. Catalyst testing

#### 3.2.1. 'Dry' tests: 1.25% O<sub>2</sub>, 0.5% CO, ~25% H<sub>2</sub>, balance N<sub>2</sub>

Fig. 3 shows the CO oxidation profile for the Pt/Al<sub>2</sub>O<sub>3</sub> as a function of catalyst temperature over the range 40–250 °C. The profile is similar to those reported in the literature for Pt/Al<sub>2</sub>O<sub>3</sub> [1,8,25–28]. There was no evidence of any methanation observed in the temperature range of our studies (40–250 °C), with complete agreement in the carbon balance between CO and CO<sub>2</sub> monitored at these temperatures. This is consistent with other workers who found no evidence of methanation below at least 250 °C [8,28].

The shape of the CO conversion curve of Pt/Al<sub>2</sub>O<sub>3</sub> is typical of that of a CO inhibited catalyst [29]. Low CO and O<sub>2</sub> conversions were observed at low temperature (with a selectivity to CO of about 40%). Oxidation of hydrogen over Pt in the absence of CO is known to be instantaneous even at room temperature [30]. Thermodynamically, CO adsorbs on noble metal surfaces more strongly than H<sub>2</sub> or O<sub>2</sub> [31–33], and in the presence of CO the Pt catalyst surface will be covered almost completely with CO at low temperature, due to its strong adsorption tendency. As a result oxidation is inhibited at low temperatures. As the temperature is increased (above 120 °C), reaction is initiated by desorption of CO, with a decrease in the surface coverage of CO and a subsequent increase in the number of surface sites available for oxygen (and hydrogen) adsorption. An increase in CO and O<sub>2</sub> conversion was observed with a further increase in temperature with complete conversion at about 200 °C for both CO and O<sub>2</sub>. Kim and Lim similarly found that the temperature for maximum CO conversion coincides with the minimum temperature for complete conversion of O<sub>2</sub> [25]. The selectivity to CO remains at 40–45%, until about 160 °C, when the oxidation of hydrogen becomes increasingly important. The selectivity then decreases to 20% at complete O<sub>2</sub> conversion, the value expected according to the CO and O<sub>2</sub> stoichiometry in the gas mixture.

Table 3

Values of  $T_{100}$  for various alumina supported M modified Pt/Al<sub>2</sub>O<sub>3</sub> catalysts (M = Cr, Mn, Fe, Co, Cu and Sn).

Catalyst	$T_{50}$ (°C)	$S_{50}$ (%)	$T_{100}$ (°C)
Pt/Al <sub>2</sub> O <sub>3</sub>	172	45	205
(1:2)CrPt/Al <sub>2</sub> O <sub>3</sub>	180	35	224
(1:2)MnPt/Al <sub>2</sub> O <sub>3</sub>	168	28	223
(1:2)FePt/Al <sub>2</sub> O <sub>3</sub>	40	100	100
(1:2)CoPt/Al <sub>2</sub> O <sub>3</sub>	38 <sup>a</sup>	49	108
(1:2)CuPt/Al <sub>2</sub> O <sub>3</sub>	115	41	157
(1:2)SnPt/Al <sub>2</sub> O <sub>3</sub>	103	50	139

<sup>a</sup> Temperature at 70% conversion.

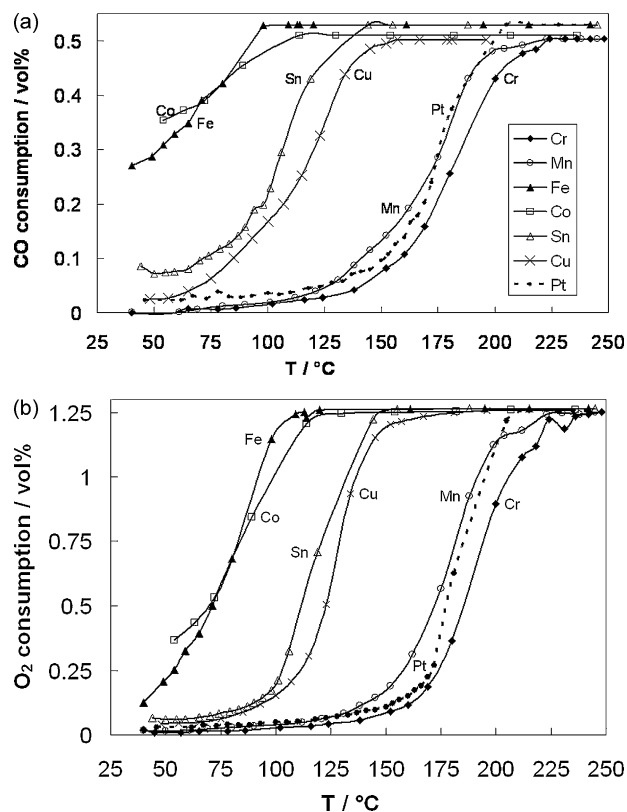


Fig. 4. Consumption of (a) CO and (b) O<sub>2</sub> as a function of temperature for the various catalysts.

Fig. 4 shows the CO and O<sub>2</sub> profiles of the (1:2)MO<sub>x</sub>/Pt/Al<sub>2</sub>O<sub>3</sub> catalysts (where M = Cr, Mn, Fe, Co, Sn and Cu), together with that of Pt/Al<sub>2</sub>O<sub>3</sub>, as a function of catalyst temperature over the range 40–250 °C. The values of temperature for complete CO conversion ( $T_{100}$ ) are given in Table 3, together with the temperature and selectivity at 50% conversion ( $T_{50}$  and  $S_{50}$  respectively).

The profiles for the different promoters are clearly very different, as are the values of  $T_{100}$  (Table 3). The Fe- and Co-modified catalysts were particularly active, with CO oxidation observed as soon as the gas mixture was introduced. 50% CO conversion was observed at 40 °C over the Fe-promoted catalyst with almost total selectivity to CO, while the Co-promoted catalyst gave almost 70% CO conversion and 50% selectivity at the same temperature. This increase in activity is particularly significant given the decrease in the accessible Pt surface sites. The Sn- and Cu-modified catalysts showed a slight improvement in the activity compared to the Pt only catalyst, with a similar CO oxidation profile but shifted to lower temperature, while there was no significant enhancement in the activities for the Cr- and Mn-modified catalysts, with a very similar profile to that of the unpromoted Pt catalyst.

The values of  $S_{50}$  and  $T_{50}$  in Table 3 and the plot of selectivity vs. conversion in Fig. 5 show that in general the more active catalysts are also more selective to CO oxidation, supporting the proposal for an additional/alternative mechanism present for these promoted catalysts. In addition to the Langmuir–Hinshelwood mechanism proposed for Pt, according to the dual-site mechanism discussed briefly in the introduction, oxygen may be dissociatively adsorbed on to the metal oxide, MO<sub>x</sub>, with oxidation of the CO at the interface between MO<sub>x</sub> and the platinum, or via the oxygen spillover to the Pt sites as discussed previously. This creates a non-competitive site for oxygen such that it no longer must compete with CO for the Pt sites. Mergler et al. [2] proposed the creation of

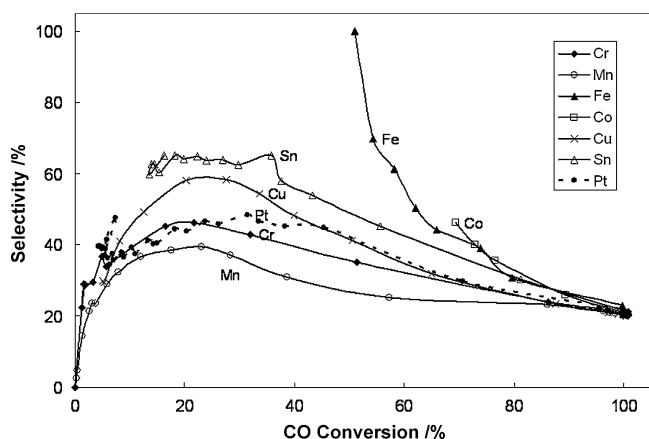


Fig. 5. The selectivity of  $O_2$  towards CO oxidation as a function of CO conversion.

O-vacancies in their Co-promoted catalysts providing suitable locations for the activation of oxygen, i.e. for the dissociation of  $O_2$ . A similar mechanism has also been proposed for Fe- and Sn-promoted catalysts [3,34]. Our results would appear to support this mechanism with the dispersed  $MO_x$  acting as an active oxygen provider. This additional mechanism would also account for the high selectivity for CO shown, for example in the value of  $S_{50}$  for the Fe-promoted catalyst. The promoted catalysts show high activities at the relatively low temperatures ( $<120^\circ C$ ) when the CO coverage on the Pt is high, thus resulting in an increase in selectivity to CO. This decreases at higher temperature (and conversion) when  $H_2$  adsorption (and subsequent oxidation) becomes more significant.

In addition, the presence of the metal oxide is likely to influence the electronic properties of the Pt metal particles. We have seen evidence of a shift in the Pt  $4f_{7/2}$  XPS peak for Pt(II) from 73.4 to 72.9 eV for a  $GeO_x/Pt/C$  catalyst prepared using the same preparation technique, suggesting that the Pt in the modified catalyst is electron-rich. A change in the electronic properties is likely to influence the strength of adsorption of the CO,  $O_2$  and/or  $H_2$ . For example, Liu et al. have reported using DRIFT studies, that Pt particles in a  $FeO_x$  promoted catalyst are electron-rich compared to those of  $Pt/Al_2O_3$  and that the CO bond of adsorbed CO is elongated [3]. Similarly, Watanabe et al. have shown that the CO bond strength is lowered by combination with Fe [22]. Komatsu and Tamura have also suggested that the CO is more weakly adsorbed for their intermetallic  $Pt_3Co$  catalyst compared to Pt alone [23]. Thus, it is possible that electronic effects (although not measured for the catalysts in this study) may also be important for the catalysts studied here. This may indeed account for some of the differences observed in the CO chemisorption results for the Fe-, Co- and Sn-promoted catalysts at higher loadings.

Whatever the mechanism, our results suggest that the controlled surface modification route used to prepare our catalysts has been successful in preparing and indeed maximising the number of interfacial Pt-oxide sites at relatively low loadings of promoter. Although enhancements in the activity and selectivity for Fe-, Co- and Sn-promoted catalysts for the PROX reaction have been reported in the literature, they are generally for catalysts with higher loadings of the promoter [3,5–7]. Our catalysts were prepared with a second metal loading of approximately 0.2 wt.%. At lower loadings, more comparable to ours, less significant effects are reported. For example, Tanaka et al. reported little promotional effect for their 1 wt.%  $Pt/Al_2O_3$  catalyst with 1 wt.%  $FeO_x$  [5,6]. Similarly, Kotobuki et al. showed little promotion for a 0.5 wt.%  $FePt/Al_2O_3$  catalyst, although they did show significant performance at loadings of 0.5 wt.% Fe for Pt supported on mordenite after heat treatment at  $300^\circ C$  [35]. Roberts et al. have however reported improved activity for their 0.5 wt.% Fe promoted  $Pt/Al_2O_3$

catalyst prepared by impregnation supported on a monolith [36]. The promotional effect of the second metal is thus clearly influenced by the preparation method of the catalyst.

The result for our Mn-modified catalyst was rather surprising as  $MnO_x$  has been reported to be an effective promoter for the CO oxidation reaction [8,11]. Ayastuy et al. have shown that promotional effects of  $MnO_x$ , in the performance of their  $MnO_x/Pt/Al_2O_3$  catalysts, depended on both the Mn content and the method of preparation [11]. They showed little promotional activity at low loading (2 wt.%), with enhanced catalytic performance only observed for their higher loaded 8 and 15 wt.% catalysts. Suh et al. however did report a significant improvement in the performance of 1 wt.%  $Pt/Al_2O_3$  for their catalyst modified with 1.8 wt.% Mn [8] but in a simulated reformat mixture in the presence of steam. ICP-AES analysis of our catalyst indicated that the Mn content of our catalyst, at 0.19 wt.%, agreed with the nominal value predicted. Thus it appears that either there is insufficient  $MnO_x$  in our catalyst to display promotional activity under these reaction conditions or that the  $MnO_x$  present on the catalyst surface is not in an active form and/or is too stable to participate in the CO oxidation actively.

As the gas mixture produced from a reformer will contain water (steam) and  $CO_2$ , a series of tests was carried out under a more realistic simulated reformat gas mixture.

### 3.2.2. 'Wet' tests: 60% $H_2$ , 20% $CO_2$ , 10% $H_2O$ , 0.1% CO, 0.15% $O_2$ , balance $N_2$

A plot of  $CO_{out}$  for the different catalysts, as a function of space velocity is shown in Fig. 6 for the catalysts in a simulated reformat mixture at  $150^\circ C$  in the presence of steam. As with the dry tests, the Fe- and Co-promoted catalysts performed significantly better than the other catalysts over the range of space velocities studied, with slightly higher performance observed for the higher loaded samples. The Mn-modified catalyst however, unlike in the dry tests, was also found to be active in this test, especially at low space velocities. The Cu-, Ni-, and in particular the Cr-modified catalysts were found to be less active than the Fe-, Co- and Mn-modified catalysts towards CO oxidation under these conditions. The Sn-promoted catalyst, as in the dry tests, was also reasonably active but showed a slightly different profile to the other promoted catalysts, with a flatter trend showing less dependence on the space velocity. This was particularly significant for the higher loaded (1:1)  $SnO_x/Pt/Al_2O_3$  catalyst which showed a decrease in activity compared to the (1:2)  $SnO_x/Pt/Al_2O_3$ , especially at lower space velocity.

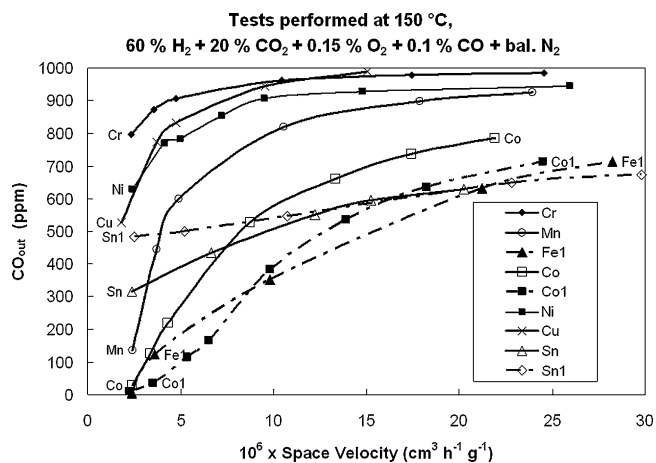


Fig. 6. Plot of  $CO_{out}$  vs. space velocity at  $150^\circ C$ , under a flowing gas mixture containing 60%  $H_2$ , 20%  $CO_2$ , 10%  $H_2O$ , 0.1% CO, 0.15%  $O_2$ , balance  $N_2$ .

The increase in  $\text{CO}_{\text{out}}$  observed with increasing space velocity may reflect mass transfer limitations in getting the reactants, particularly oxygen, to the catalyst surface at higher flow rates. It is envisaged that at higher flow rates, the ability of oxygen from the gas phase to regenerate the active oxygen, by reoxidation of the oxide, is likely to be impaired. The Sn-promoted catalysts appears to be more immune to space velocity effects, suggesting that they may be less sensitive to mass transport effects such as the oxygen supply. It is also possible that the Sn-promoted catalysts may be particularly susceptible to poisoning by the excess  $\text{CO}_2$  or  $\text{H}_2\text{O}$  (OH) present in the simulated reformat mixture, reflected in the lower activity at low space velocity observed for these catalysts, especially at higher loading.

The enhancement in the CO oxidation observed for the Mn-modified catalyst in the simulated reformat mixture containing steam (and  $\text{CO}_2$ ) but not the dry tests, suggests that the  $\text{MnO}_x$  is now acting as a promoter for the reaction. Given that the simulated mixture contains water (steam) it is possible that surface OH species may play a part, either in the mechanism directly as has been proposed by a number of authors [8–10] or in the form of the Mn species itself, such that the  $\text{MnO}_x$  can now act as a source of active oxygen. Mn oxides can assume a wide range of simple and mixed compositions with Mn atoms in different oxidation states, important for redox catalysts [37]. Whatever the nature of the Mn species, it does appear that the  $\text{MnO}_x$  is a promoter for Pt for the PROX reaction in the wet test, and this is likely to reflect its oxidation state and redox properties under the conditions used.

It has been reported in the literature that the oxidation state of the promoting oxide is indeed important. For example, a partially reduced metal oxide was reported to be necessary to increase the activity of the Pt catalyst by Mergler et al. for their  $\text{CoO}_x$  promoted catalysts [2]. Similarly, Meunier et al. found that  $\text{Co}^{2+}$  ions in a Pt/ $\text{CoO}_x/\text{Al}_2\text{O}_3$  catalyst dissociate oxygen more easily than  $\text{Co}^{3+}$  [38]. Sirijaruphan et al. have also shown that oxidation of their promoter,  $\text{FeO}_x$ , during the PROX reaction is a significant cause of deactivation for their  $\text{FeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalysts [4]. The Pt itself is likely to play a role in aiding reduction of the promoter, as shown by our EPR and XANES studies of related catalysts and by Ayastuy et al. who reported for their  $\text{MnO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalysts that reduction of the Mn was found to be facilitated by the Pt [11].

Due to the nature of the dual-site mechanism, the performance of a promoting oxide will depend on its ability to provide active oxygen to the reaction and undergo reoxidation by oxygen from the gas phase. This in turn is likely to reflect the capacity of the promoter to form and move easily between different oxidation states and the mobility of oxygen/oxygen vacancies. This is likely to account, at least in part, for the differences we observe for the different metals. In addition, effects of the modifying metal oxide on the electronic properties of Pt may also be important, influencing the adsorption properties of the reactant gases on the Pt. Under the conditions used in our work, it is Fe and Co of the first transition metal series that appear to exist in a form most able to promote the PROX reaction and to supply the active oxygen to the Pt.  $\text{MnO}_x$  is also a promoter under selected conditions, apparently dependent on the nature and possibly the oxidation state of the oxide present. Sn similarly is an active promoter, possibly via the same mechanism, however slight differences are evident in its behaviour, in particular in the presence of excess  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Cu and Ni show some promotional activity under the experimental conditions used in our studies. Cr however does not appear to be present in a suitable form in our catalyst to take part in this redox mechanism. It is also possibly not associated with the Pt or in too low a concentration (reflected in the less successful preparation of this catalyst) to act as a promoter.

## 4. Conclusions

Our results have shown by utilising a controlled surface reaction between the Pt surface and a precursor of a promoting oxide that significant enhancements in both the activity and selectivity can be seen at low loadings (0.15–0.25 wt.%) of the promoter. The selective nature of the deposition and the ability to build Pt:promoter oxide interfacial sites at low loadings using this technique, highlights the importance of the Pt–metal oxide interface, supporting the proposed dual-site mechanism. Of the elements tested the promotional activities appear to follow the trend  $\text{Co} \approx \text{Fe} > \text{Mn} > \text{Sn} \approx \text{Cu} \approx \text{Ni} > \text{Cr}$ . The differences observed for the different metals suggest that the nature of the oxide may play a significant role in determining whether a metal oxide will act as a promoter or not.

## Acknowledgements

This work was supported by The Open University (OU) and the Johnson Matthey Technology Centre (JMTC). We would like to thank Gregory Goodlet (JMTC) for his help with the electron microscopy and Graham Jeffs (OU) for help with the catalyst testing. Finally, we would like to thank Dr. Valerie Self for her input to the project.

## References

- [1] O. Korotkikh, R. Farrauto, *Catal. Today* 62 (2000) 249.
- [2] Y.J. Mergler, A. van Aalst, J. van Delft, B.E. Nieuwenhuys, *Appl. Catal. B: Environ.* 10 (1996) 245.
- [3] X. Liu, O. Korotkikh, R. Farrauto, *Appl. Catal. A: Gen.* 226 (2002) 293.
- [4] A. Sirijaruphan, J.G. Goodwin Jr., R.W. Rice, *J. Catal.* 224 (2004) 304.
- [5] M. Shou, K. Tanaka, K. Yoshioka, Y. Moro-oka, S. Nagano, *Catal. Today* 90 (2004) 255.
- [6] K. Tanaka, Y. Moro-oka, K. Ishigure, T. Yajima, Y. Okabe, Y. Kato, H. Hamano, S. Sekiya, H. Tanaka, Y. Matsumoto, H. Koinuma, H. He, C. Zhang, Q. Feng, *Catal. Lett.* 92 (Nos. 3–4) (2004) 115.
- [7] K. Tanaka, M. Shou, H. He, X. Suh, *Catal. Lett.* 110 (Nos. 3–4) (2006) 185.
- [8] D.J. Suh, C. Kwak, J.-H. Kim, S.M. Kwon, T.-J. Park, *J. Power Sources* 142 (2005) 70.
- [9] O. Podznyakova, D. Teschner, A. Wootsch, J. Kröhnert, B. Steinhauer, H. Sauer, L. Toth, F.C. Jentoft, A. Knop-Gericke, Z. Paál, R. Schlögl, *J. Catal.* 237 (2006) 1.
- [10] O. Podznyakova-Tellinger, D. Teschner, J. Kröhnert, F.C. Jentoft, A. Knop-Gericke, R. Schlögl, A. Wootsch, *J. Phys. Chem. C* 111 (2007) 5426.
- [11] J.L. Ayastuy, M.P. Gonzalez-Marcos, J.R. Gonzalez-Velasco, M.A. Gutierrez-Ortiz, *Appl. Catal. B: Environ.* 70 (2007) 532.
- [12] E.-Y. Ko, E.D. Park, K.W. Seo, H.C. Lee, D. Lee, S. Kim, *Catal. Today* 116 (2006) 377.
- [13] V. Caps, S. Arrii, F. Morfin, G. Bergeret, J.-L. Rousset, *Faraday Trans.* 138 (2008) 241.
- [14] E.M. Crabb, R. Marshall, *Appl. Catal. A: Gen.* 217 (2001) 41.
- [15] E.M. Crabb, R. Marshall, D. Thompson, *J. Electrochem. Soc.* 147 (12) (2000) 4440.
- [16] E.M. Crabb, M.K. Ravikumar, *Electrochim. Acta* 46 (2001) 1033.
- [17] E.M. Crabb, M.K. Ravikumar, Y. Qian, A.E. Russell, S. Maniguet, J. Yao, D. Thompson, M. Hurford, S.C. Ball, *Electrochem. Solid State Lett.* 5 (1) (2002) A5.
- [18] Peter Wells, Ph.D. Thesis, University of Southampton, 2007.
- [19] E. Merlen, P. Beccat, J.C. Bertolini, P. Delichère, N. Zanier, B. Didillon, *J. Catal.* 159 (1996) 178.
- [20] F. Humblot, D. Didillon, F. Lepeltier, J.P. Candy, J. Corker, O. Clause, F. Bayard, J.M. Basset, *J. Am. Chem. Soc.* 120 (1998) 137.
- [21] F. Humblot, J.P. Candy, F. Le Peltier, B. Didillon, J.M. Basset, *J. Catal.* 179 (1998) 459.
- [22] M. Watanabe, H. Uchida, K. Ohkubo, H. Igarashi, *Appl. Catal. B: Environ.* 46 (2003) 595.
- [23] T. Komatsu, A. Tamura, *J. Catal.* 258 (2008) 306.
- [24] M.C. Sánchez Sierra, R.G. Ruiz, M.G. Proietti, J. Blanco, *J. Mol. Catal. A: Chem.* 108 (1996) 178.
- [25] H. Kim, M. Lim, *Appl. Catal. A: Gen.* 224 (2002) 27.
- [26] S. Oh, R. Sinkevitch, *J. Catal.* 142 (1993) 254.
- [27] A. Manasilp, E. Gulari, *Appl. Catal. B: Environ.* 37 (2002) 17.
- [28] M. Kahlisch, H. Gasteiger, R. Behm, *J. Catal.* 171 (1997) 93.
- [29] B.E. Nieuwenhuys, *Adv. Catal.* 44 (1999) 259.
- [30] S. Völkening, K. Bedürftig, K. Jacobi, J. Wintterlin, G. Ertl, *Phys. Rev. Lett.* 83 (1999) 2672.
- [31] T. Engel, G. Ertl, in: W.G. Frankenburg, V.I. Komarewsky, E.K. Rideal (Eds.), *Advances in Catalysis*, vol. 28, Academic Press, NY, 1979, p. 1.
- [32] S.H. Oh, G.B. Fisher, J.E. Carpenter, D.W. Goodman, *J. Catal.* 100 (1986) 360.
- [33] Y. Nishiyama, H. Wise, *J. Catal.* 32 (1974) 50.
- [34] M.M. Schubert, M.J. Kahlisch, G. Feldmeyer, M. Hüttner, S. Hackenberg, H.A. Gasteiger, R.J. Behm, *PCCP* 3 (2001) 1123.
- [35] M. Kotobuki, A. Watanabe, H. Uchida, H. Yamashita, M. Watanabe, *Appl. Catal. A: Gen.* 307 (2006) 275.
- [36] G.W. Roberts, P. Chin, X. Sun, J.J. Spivey, *Appl. Catal. B: Environ.* 46 (2003) 601.
- [37] C. Zener, *Phys. Rev.* 81 (4) (1951) 440.
- [38] G. Meunier, F. Garin, J. Schmitt, G. Maire, R. Roche, *Stud. Surf. Sci. Catal.* 30 (1987) 24.